

# PATENT COOPERATION TREATY

## PCT

### INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY


(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

REC'D 09 DEC 2005

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Applicant's or agent's file reference BW341R/RAB		<b>FOR FURTHER ACTION</b>		See Form PCT/PEAA416
International application No. PCT/IB2004/052230		International filing date (day/month/year) 28.10.2004	Priority date (day/month/year) 29.10.2003	
International Patent Classification (IPC) or national classification and IPC B01J37/03, B01J23/46, C07C45/38, C07C45/39				
Applicant CONSIGLIO NAZIONALE DELLE RICERCHE et al.				
<p>1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 6 sheets, including this cover sheet.</p> <p>3. This report is also accompanied by ANNEXES, comprising:</p> <p>a. <input checked="" type="checkbox"/> sent to the applicant and to the International Bureau a total of 3 sheets, as follows:</p> <p><input checked="" type="checkbox"/> sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).</p> <p><input type="checkbox"/> sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.</p> <p>b. <input type="checkbox"/> (sent to the International Bureau only) a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing and/or tables related thereto, in computer readable form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).</p>				
<p>4. This report contains indications relating to the following items:</p> <p><input checked="" type="checkbox"/> Box No. I Basis of the opinion</p> <p><input type="checkbox"/> Box No. II Priority</p> <p><input type="checkbox"/> Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</p> <p><input checked="" type="checkbox"/> Box No. IV Lack of unity of invention</p> <p><input checked="" type="checkbox"/> Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</p> <p><input type="checkbox"/> Box No. VI Certain documents cited</p> <p><input checked="" type="checkbox"/> Box No. VII Certain defects in the international application</p> <p><input type="checkbox"/> Box No. VIII Certain observations on the international application</p>				
Date of submission of the demand 30.09.2005		Date of completion of this report 08.12.2005		
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465		Authorized Officer Bork, A-M Telephone No. +49 89 2399-8311		



**INTERNATIONAL PRELIMINARY REPORT  
ON PATENTABILITY**

International application No.  
PCT/IB2004/052230

**Box No. I Basis of the report**

1. With regard to the **language**, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.
- ☐ This report is based on translations from the original language into the following language , which is the language of a translation furnished for the purposes of:
- ☐ international search (under Rules 12.3 and 23.1(b))
  - ☐ publication of the international application (under Rule 12.4)
  - ☐ international preliminary examination (under Rules 55.2 and/or 55.3)
2. With regard to the **elements\*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report):*

**Description, Pages**

1-25 as originally filed

**Claims, Numbers**

1-9, 13-25 received on 04.10.2005 with letter of 30.09.2005

**Drawings, Sheets**

1/2, 2/2 as originally filed

- ☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing
3. ☒ The amendments have resulted in the cancellation of:
- ☐ the description, pages
  - ☒ the claims, Nos. 10-13,21,22
  - ☐ the drawings, sheets/figs
  - ☐ the sequence listing *(specify):*
  - ☐ any table(s) related to sequence listing *(specify):*
4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).
- ☐ the description, pages
  - ☐ the claims, Nos.
  - ☐ the drawings, sheets/figs
  - ☐ the sequence listing *(specify):*
  - ☐ any table(s) related to sequence listing *(specify):*

\* If item 4 applies, some or all of these sheets may be marked "superseded."

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**Box No. IV Lack of unity of invention**

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1. ☒ In response to the invitation to restrict or pay additional fees, the applicant has:
- ☒ restricted the claims.
  - ☒ paid additional fees.
  - ☐ paid additional fees under protest.
  - ☐ neither restricted nor paid additional fees.
2. ☐ This Authority found that the requirement of unity of invention is not complied with and chose, according to Rule 68.1, not to invite the applicant to restrict or pay additional fees.
3. This Authority considers that the requirement of unity of invention in accordance with Rules 13.1, 13.2 and 13.3 is
- ☐ complied with.
  - ☒ not complied with for the following reasons:  
**see separate sheet**
4. Consequently, this report has been established in respect of the following parts of the international application:
- ☐ all parts.
  - ☒ the parts relating to claims Nos. 1-9,13-25 .

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**Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

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1. Statement

Novelty (N)	Yes: Claims	1-9,13-24
	No: Claims	25
Inventive step (IS)	Yes: Claims	1-9,13-24
	No: Claims	25
Industrial applicability (IA)	Yes: Claims	1-9,13-25
	No: Claims	

2. Citations and explanations (Rule 70.7):

**see separate sheet**

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**Box No. VII Certain defects in the international application**

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The following defects in the form or contents of the international application have been noted:

**see separate sheet**

**INTERNATIONAL PRELIMINARY  
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(SEPARATE SHEET)**

International application No.

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In view of the objection of lack of unity (Rule 13.1 PCT) (see the search report) the applicant restricted his application to the first invention mentioned in the search report.

The present international preliminary report is based on the amended claims 1-9,13-25.

**Re Item V.**

1. The following documents are referred to in this communication:

D1 : PAGLIARO M ET AL., TETRAHEDRON LETTERS, vol. 42, no. 27,  
(2001-07-02), pages 4511-4514

D2 : BLELOCH, A. ET AL., CHEM. COMMUN., 1999, pages 1907-1908

2. Novelty

a) Claim 25 refers to well-known compounds which are not patentable (PCT Guidelines, 5.26 -5.27).

b) Document **D1** discloses (page 4512, left-hand column, paragraph 3 - page 4513, right-hand column, paragraph 2; page 4514, reference 12) catalysts for the aerobic oxidation of alcohols. The catalysts are organically modified silicas (ormosils) doped with tetra-n-propylammonium perruthenate (TPAP) prepared by copolymerisation of  $\text{Si}(\text{OCH}_3)_4$  with  $\text{CH}_3\text{Si}(\text{OCH}_3)_3$  at various ratios in the presence of TPAP,  $\text{H}_2\text{O}$  and  $\text{CH}_3\text{OH}$ , via the sol-gel process.

The subject-matter of independent claim 1 differs from the disclosure of D1 in that the copolymerisation is carried out with a fluorinated organosilane (instead of alkyl organosilane  $\text{CH}_3\text{Si}(\text{OCH}_3)_3$  in D1).

Document **D2** discloses (pages 1907-1908) mesoporous silicate MCM-41 doped with TPAP, in which the perruthenate anions are ionically bound at the internal surface of the silica mesopores as heterogenous catalysts for the aerobic oxidation of alcohols.

From this, the subject-matter of independent claim 1 differs in that the TPAP are entrapped in a matrix prepared from fluorinated organosilane via the sol-gel process.

In view of D1 and D2 the subject matter of the application can be regarded as novel and meet the requirements of Article 33(1) and 33(2) PCT.

### 3. Inventive Step

D1 is to be considered as the closest prior art and in view of its contents the technical problem to be solved by the present application may be regarded as providing new organically modified silicas doped with tetra-n-propylammonium perruthenate (TPAP) as catalysts for the aerobic oxidation of alcohols.

The solution of this problem provided by the present application are the catalytic materials according to present claim 13 and produced according to claim 1 with said distinguishing feature (copolymerisation of  $\text{Si}(\text{OCH}_3)_4$  with a fluorinated organosilane).

Since the solution of the technical problem is neither disclosed, nor suggested in the prior art and in view of the comparative examples showing the better catalytic effect of the TPAP entrapped in the fluorinated matrix vs. a methylated matrix, the subject-matter of the present application according to claims 1-9, 13-24, provided that these claims are corrected taking into account the observation under point VII, can be regarded as inventive (Art. 33(3) PCT).

### Re Item VII.

- a) Claim 3 seems to depend on claim 1 and not on claim 2 as indicated, since claim 2 make reference to metal alkoxides.
- b) Claim 4 is not clear because it made reference to a compound of the formula ' $n\text{R-Si}(\text{OCH}_3)_3$  wherein n is 1'. If n is 1, it makes no sense to indicate it. Moreover, lack of clarity appears because of the definition '**R** represents (3,fluorotrimetoxysilane)' and because of the wording 'to form a perfluoroalkyl group' since the groups indicated are not perfluoroalkyl groups.
- c) Present claims 13-25 should be renumbering as claims 10-20.
- d) The description is not in conformity with the claims as required by Rule 5.1(a)(iii) PCT.

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## CLAIMS

1. A process for the production of nanohybrid sol-gel materials for the heterogeneous aerobic catalysis containing tetra-n-propylammonium perruthenate (TPAP) entrapped in the matrix, obtained via a sol-gel process by hydrolysis and co-polymerization of organosilanes and of silanes in the presence of said tetra-n-propylammonium perruthenate (TPAP), water and an organic cosolvent, characterized in that

said co-polymerization is carried out with a precursor fluorinated organosilane and a non-fluorinated silane monomer.

2. The process according to claim 1, wherein said fluorinated organosilane and said silane are in the form of metal alkoxides.

3. The process according to claim 2, wherein said precursor fluorinated organosilane is a fluorinated silica alkoxide,

or a fluorinated organosilane.

4. The process according to claim 3, wherein said fluorinated silica alkoxide is a compound of the formula  $nR-Si(OCH_3)_3$

wherein n is 1 and R represents:

(3,fluorotrimethoxysilane),

a fluorinated alkyl chain  $CF_3(CH_2)_2-$ ,  $CF_3(CF_2)_7CH_2CH_2-$ , or  $CF_3(CF_2)_5CH_2CH_2-$ , to form a perfluoroalkyl group,

5. The process according to claim 3, wherein said fluorinated organosilanes have the formula  $RR'Si(OCH_3)_2$  wherein R has the meaning indicated in claim 4 and R' is any one non-hydrolyzable substituent organic group.

6. The process according to claim 5, wherein said non-hydrolyzable substituent organic group is  $CH_3-$ ,  $CH_3CH_2-$ ,  $CH_3CH_2CH_2-$ .

7. The process according to claim 1, wherein said non-fluorinated silane monomer is  $Si(OCH_3)_4$  (TMOS),

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Si(OCH<sub>2</sub>CH<sub>3</sub>)<sub>4</sub> (TEOS) or mixtures thereof.

8. The process according to claim 1, wherein said cosolvent is methanol, ethanol, propanol or a combination thereof.

9. The process according to any of the claims 1 to 8, wherein the molar ratio (Si:MeOH:H<sub>2</sub>O) molar ratio among the total silica (Si) (fluorinated organosilane + silane), amount of cosolvent (MeOH), and amount of water (H<sub>2</sub>O), is selected so as to utilize elevated stoichiometric values, both of water and of cosolvent, of 1:8:4, so that the resulting hydrophobic matrices of said catalysts exhibit particular reactivity.

13. A nanohybrid sol-gel catalytic material, based on silica organically modified and doped with the ruthenium species tetra-n-propylammonium perruthenate (TPAP) produced via a process as claimed in claims 1 to 9.

14. Use of a nanohybrid sol-gel material, based on silica organically modified and doped with the ruthenium species tetra-n-propylammonium perruthenate (TPAP) as claimed in claim 13, for use as catalyst having a highly efficient hydrophobic matrix for the selective aerobic oxidation of alcohols to carbonyls with oxygen at atmospheric pressure in a solvent.

15. The use of a material according to claim 14, wherein said solvent is carbon dioxide in supercritical state.

16. The use of a material according to claim 14, wherein said solvent is an organic solvent.

17. The use of a material according to claim 16, wherein said solvent is toluene or dichloromethane.

18. A process for the selective heterogeneous aerobic catalytic oxidation of alcohols to carbonyls in a solvent, wherein, as catalyst, it is employed a nanohybrid sol-gel material based on silica organically modified and doped with the ruthenium species tetra-n-propylammonium perruthenate (TPAP), as claimed in claim



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13, and as solvent in the reaction of said catalytic oxidation it is employed carbon dioxide in supercritical state.

5 19. The process according to claim 18, wherein, as primary oxidant, it is employed oxygen at atmospheric pressure.

10 20. The process according to claim 18 or 19, wherein during the catalytic oxidation the temperature of the supercritical carbon dioxide is kept within a range of from 50° to 120°C at a pressure of from 70 to 240 bar, and the partial pressure of the oxygen is kept at a few bars, and in particular in the neighborhood of the value of 1 bar.

15 23. The process according to any of the claims 18 to 20 for the heterogeneous aerobic oxidation of benzyl alcohol, 1-phenylethanol, cyclohexanol, 1-octanol, trans-cinnamyl alcohol.

20 24. Nanohybrid sol-gel catalyst for the heterogeneous aerobic catalysis containing tetra-n-propylammonium perruthenate (TPAP) entrapped in the sol-gel matrix obtained by a process as claimed in any one of claims 1 to 9.

25. Alcohol oxidation product obtained by a process as claimed in any one of claims 18 to 20.